

Neutron Activation Analysis of Thorium by the Use of the Japan Materials Testing Reactor

著者	Mitsugashira Toshiaki, Koma Yoshikazu, Hirai Shoji, Okada Yukiko
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	35
number	2
page range	256-260
year	1991-03-05
URL	http://hdl.handle.net/10097/28344

Neutron Activation Analysis of Thorium by the Use of the Japan
Materials Testing Reactor*

Toshiaki Mitsugashira**, Yoshikazu Koma**,
Shoji Hirai***, and Yukiko Okada***

(Received January 20, 1991)

Synopsis

Hydraulic power rabbit in the Japan Materials Testing Reactor (JMTR) was used for highly sensitive neutron activation analysis of thorium in silica and aluminum. The thermal neutron flux of JMTR is higher than 1×10^{14} n/cm²/sec. A number of radioactive isotopes were made from impurities of high purity aluminum and silica irradiated in JMTR. ¹⁸³Ta, which was produced from ¹⁸¹Ta by (2n, γ) reaction, was observed and made the determination of thorium difficult. The objective activation products ²³³Pa for the determination of thorium was isolated from majority of interfering radioactivity by a method combined with anion exchange and LaF₃ coprecipitation.

It was found that the detection limit of thorium was less than 2×10^{-13} g. The method is useful to the analysis for thorium in high purity aluminum and silica that might be used to make very large scale integrated circuit.

I. Introduction

It is well known that traces of α -active radioisotopes in semiconductor materials may destroy the function of large scale integrated circuit by internal irradiation. Therefore, the analytical method for uranium and thorium with highest sensitivity is necessary to develop a preparative method for semiconductor materials.

Neutron activation analysis seems promising for highly sensitive analysis of uranium and thorium.^{1, 3)} The activation product from uranium is ²³⁹Np and that from thorium is ²³³Pa, respectively.

* The 1858th report of Institute for Materials Research.

**Institute for Materials Research, Tohoku University, Sendai 980

***Atomic Energy Research Laboratory, Musashi Institute of Technology,
Kawasaki 215

The determination of uranium and thorium through the gamma-emission rates of ^{239}Np and ^{233}Pa will be performed easily by the use of gamma-ray spectrometric technique. Undoubtedly, the use of high flux reactor for activation and long irradiation favor the enhancement of the sensitivity. But, on the other hand, a number of interfering gamma-emitters were produced simultaneously from impurities. Considering the half-life values of ^{239}Np and ^{233}Pa , the effect of long and high flux irradiation seems to be more typical for the detection of ^{233}Pa . The objective of this report is focussed on the examination of the chemical method to separate ^{233}Pa , which was proposed in Ref.4, for the determination of thorium in semiconductor grade silica and aluminum irradiated in a high flux reactor and to examine the effect of the usage of JMTR for the activation.

II. Experimental

1. Irradiation.

The silica samples used were calcined products of hydrolyzed silane and the aluminum samples were triply zone refined products. All samples were supplied from semiconductor companies. About 300mg of each sample was encapsulated in a small quartz tube separately under reduced pressure and the quartz tubes were encapsulated again in another quartz tube of 16mm ϕ x 60mm with about 10^5 Pa of He.

The hydraulic power rabbit I and II were used for activation. The thermal neutron flux in the hydraulic power rabbits exceeds $1 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. Silica powder and aluminum rod samples were always irradiated together with 10^{-6} g of Th as standard.

2. Chemical separation

Irradiated silica was dissolved into a HF solution and evaporated to dryness in a teflon beaker. Silicon was removed by evaporation as SiF_4 . The residue was dissolved in a 10ml aliquot of a 9M (mol/dm³) HCl. About 100mg of non-irradiated aluminum was dissolved in this solution to mask traces of F^- remained.

Irradiated aluminum rod

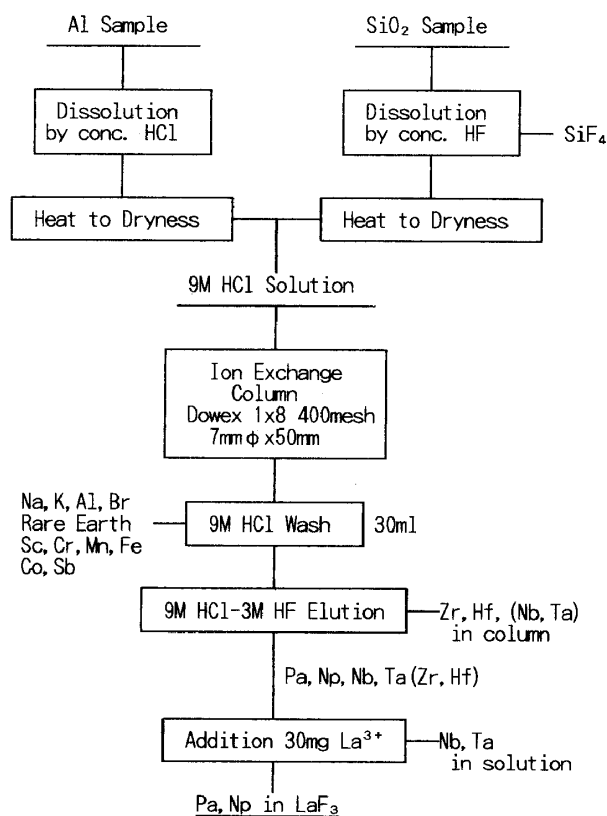


Fig.1. Scheme of Chemical Separation

samples were dissolved in 9M HCl solution containing traces of Ni^{2+} .

^{233}Pa was adsorbed on an anion exchange column. The column was washed by 9M HCl solution to remove majority of activation products. ^{233}Pa was eluted out with 20 ml of 9M HCl-3M HF solution (the solution is called as an anion exchanged fraction hereafter).

Then, ^{233}Pa was coprecipitated with LaF_3 by the addition of 30 mg of La^{3+} . (coprecipitated fraction) The outline of the separation procedure is shown in Fig. 1.

3. Gamma-ray spectrometry

A coaxial hyper-pure Ge detector and a well-type Ge detector were used to take a gamma-ray spectrum. The effective volume of the detectors exceeds 80cm^3 . A 4096 ch. PHA combined with a personal computer was used to take gamma-ray spectrum.

A computer program based on least square fitting was used to calculate gamma-ray peak intensity of the observed spectrum.

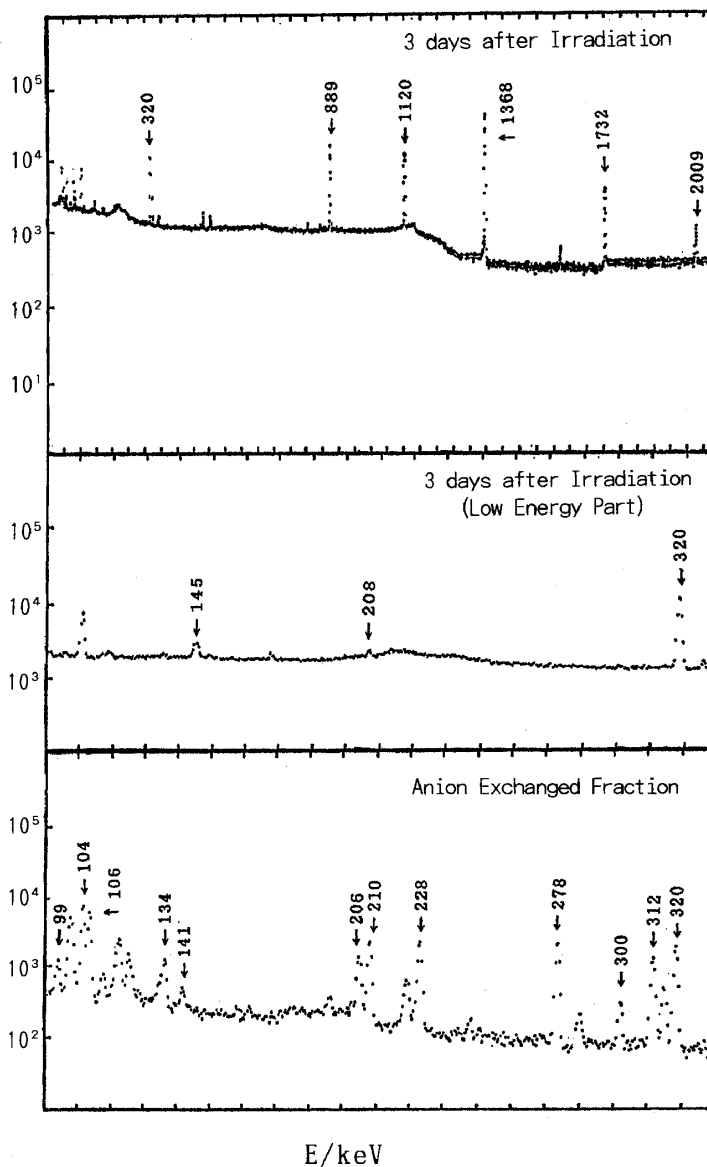


Fig.2 Gamma-ray spectra of high purity aluminum irradiated for 120 hours and the anion exchanged fraction. The values in the figure indicate gamma-ray energy.

III. Results and Discussion

Fig. 2 illustrates gamma-ray spectra of high purity aluminum irradiated for 120 hours together with that of anion exchanged

fraction. Numbers of gamma-emitters produced from impurities were effectively removed by the wash with 9M HCl solution. ^{51}Cr , ^{72}Ga , ^{59}Fe , ^{60}Co , ^{65}Zn , ^{95}Zr , and ^{95}Nb were absorbed strongly on the column and remained in the column after the elution. In Fig 3, a gamma-ray spectrum of anion exchanged fraction was compared with coprecipitated fraction. As is valid by 153, 222, 246, and 313 keV gamma-rays, ^{182}Ta and ^{183}Ta found in the anion exchanged fraction were removed from coprecipitated fraction.

The effect of chemical separation is summarized in Table 1. As is shown in Table 1, coprecipitation is necessary to remove Na, K, Zr, Nb, Mo, Sb, Hf, and Ta and anion exchange is effective to remove Sc, Cr, Mn, Fe, Co, Mo, Sb, and La as well as Na and K.

^{183}Ta is formed by double neutron capture reaction of ^{181}Ta . The large neutron capture cross section of ^{182}Ta favors the formation of ^{183}Ta . The radioactivity ratio ($^{183}\text{Ta}/^{182}\text{Ta}$) is roughly proportional to irradiation time and neutron flux. The calculated ratio is 2.0 for 120 hours irradiation in JMTR ($\phi = 10^{14} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) and the value is consistent with the present experimental result. Double capture reaction becomes more significant in the activation by high flux neutrons.

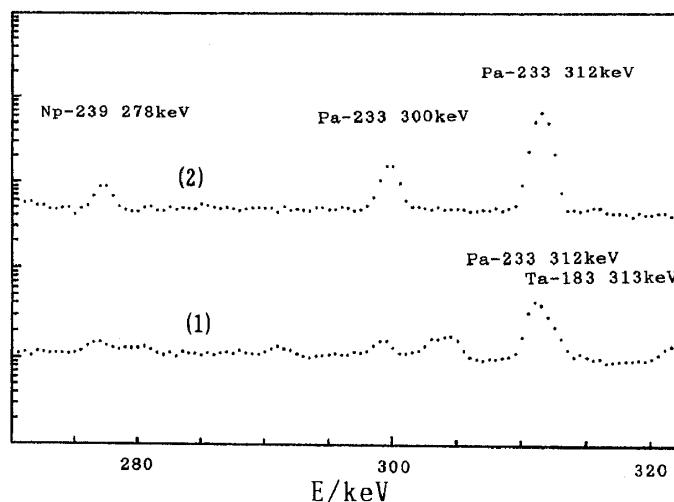


Fig.3. Gamma-ray spectra of anion exchanged fraction (1) and coprecipitated fraction (2) obtained from high purity aluminum irradiated for 120 hours.

Table 1. Chemical yields of activation products on the separation process.

Nuclides	Anion exchanged fraction	Coprecipitated fraction
^{24}Na	$\sim 10^{-4}$	$< 10^{-9}$
^{42}K	$\sim 10^{-4}$	$< 10^{-9}$
^{52}Cr	$\sim 10^{-5}$	$< 10^{-8}$
^{54}Mn	$< 10^{-5}$	$< 10^{-8}$
^{59}Fe	$< 10^{-5}$	$< 10^{-8}$
^{60}Co	$< 10^{-5}$	$< 10^{-8}$
^{46}Sc	$< 10^{-6}$	$< 10^{-7}$
^{95}Zr	~ 0.1	$< 10^{-6}$
^{95}Nb	~ 0.1	$< 10^{-6}$
^{99}Mo	$< 10^{-4}$	$< 10^{-7}$
^{124}Sb	$< 10^{-4}$	$< 10^{-8}$
^{140}La	$< 10^{-8}$	$< 10^{-8}$
^{181}Hf	$< 10^{-4}$	$< 10^{-8}$
^{182}Ta	~ 0.5	$< 10^{-6}$
^{233}Pa	1.0 ± 0.1	1.0 ± 0.05
^{239}Np	1.0 ± 0.1	1.0 ± 0.03

It should be remembered that we concern the analysis of very low content of thorium. Samples to be used for analysis must be the highest grade of purity. That is, it is not always possible to know previously about impurities which interferes the detection of objective gamma-rays.

The detection limit of neutron activation analysis is enhanced in proportion to the amount of the sample irradiated (S), neutron flux (f), irradiation time (t), time for the spectrum accumulation (T) and the detection efficiency of the detector (ϵ). The background counts around the gamma-peak (BG) also affects the detection limit and should be minimized by chemical separation. As is shown in Fig. 3, ^{239}Np was a main interfering gamma-emitters that contributed to the increase in BG of coprecipitated fraction. The time elapsed from the end of the irradiation was selected around 20 days to wait for the decay of ^{239}Np without appreciable decrease of the signals from ^{233}Pa . In the present irradiation condition, i.e., $t=120\text{h}$ and $f=10^{14}\text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, typical value of activation yields for ^{233}Pa was about $2\times 10^{11}\text{Bq/gTh}$. The limit for the gamma-peak detection, defined by $3(2\text{BG})^{1/2}$ around 312keV peak in the spectra of coprecipitated fractions obtained from the highest grade of silica and aluminum, was about $4\times 10^{-3}\text{cps}$ at $T=10000\text{s}$. The value corresponds to $4\times 10^{-2}\text{Bq}$ of ^{233}Pa . Thus, the overall detection limit for Th was found to be about $2\times 10^{-13}\text{g}$.

The limit corresponds to the sensitivity of about 1 ppt for thorium. The values of S (300mg), f, ϵ (0.27), and T seem to be practically the largest. This fact implies that the detection limit given above was almost critical and that the value was mainly determined by the chemical separation procedures.

References

- (1) S. Fakhi, J.M. Paulus, S. Bouhlassa, J. Radioanal. Nucl. Chem., 121(1988), 99. and 109.
- (2) N. Kurashima, Master Thesis. Musashi Institute for Technology, 1990.
- (3) Y. Hayakawa, Master Thesis. Musashi Institute for Technology, 1986.
- (4) T. Mitsugashira, Y. Koma, S. Hirai, Y. Okada, N. Kurashima, and H. Sakurai, J. Radioanal. Nucl. Chem., 143(1990), 531.